found necessary for complete purification to boil the crude fluorenone with a trace of stannous chloride in hydrochloric acid. The product then crystallized from alcohol in small yellow plates, m. p. 150–152°. From the alkaline extracts a small quantity of **2-hydroxy-3-naphthyl phenyl ketone** separated on acidification. This crystallized from alcohol in golden yellow leaflets, m. p. 156°.

Anal. Calcd. for $C_{17}H_{13}O_2$: C, 81.91; H, 5.22. Found: C, 82.29; H, 5.05.

When the naphthoxazone V was treated with benzylmagnesium chloride none of the desired **2-acetamido-3-naphthylbenzyl ketone** was obtained. However a small yield of **2-acetamido-3-naphthyldibenzylcarbinol** did result and the product melting at 181° crystallized from acetone-alcohol in colorless prisms.

Anal. Calcd. for $C_{27}H_{25}O_2N$: C, 82.03; H, 6.33; N, 3.54. Found: C, 81.97; H, 6.39; N, 3.22.

2-Acetamido-3-naphthyl 2′-naphthyl ketone (VI) was obtained in very impure condition by the action of 2-naphthylmagnesium bromide on V following the usual procedures. A small sample after repeated crystallizations from methanol was finally obtained as white needles, m. p. 169°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 81.37; H, 5.05; N, 4.12. Found: C, 81.80; H, 5.18; N, 3.98.

Hydrolysis of the bulk of the above amide effected the removal of a large quantity of tarry by-products and gave a 4% yield based on the 2-bromonaphthalene used. The **2-amino-3-naphthyl 2′-naphthyl ketone** formed crystallized from alcohol in fine orange-yellow needles; m. p. 154–156°.

Anal. Calcd. for $C_{21}H_{15}ON$: C, 84.83; H, 5.09; N, 4.71. Found: C, 84.91; H, 5.26; N, 4.72.

2,3,5,6-Dibenzofluorenone.—From 0.5 g. of the above amine by the usual diazotization procedure, a product (0.1 g.) was obtained which crystallized from glacial acetic acid in small orange-yellow leaflets, m. p. 185°.

Anal. Calcd. for $C_{21}H_{12}O$: C, 90.00; H, 4.32. Found: C, 90.10; H, 4.14.

As a by-product 25 mg. of alkali-soluble material resulted, which likewise crystallized from glacial acetic acid in small golden needles, m. p. 139°. This was evidently **2-hydroxy-3-naphthyl 2′-naphthyl ketone.**

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.55; H, 4.73. Found: C, 84.30; H, 5.07.

The attempted reduction of the dibenzofluorenone by red phosphorus and hydriodic acid produced no results after over a week's refluxing.

In all of the described Grignard reactions varying amounts of the oxazone were recovered as the free acetyl amino acid. The yields have been calculated however on the basis of the original quantities used.

Summary

A new modification of the Ullmann synthesis of fluorene derivatives has been described. Three new fluorene derivatives: 1-methylfluorenone, 1-methylfluorene and 2,3,5,6-dibenzofluorenone have been described together with numerous intermediates. The synthesis has also been applied to the preparation of several previously reported compounds.

Although the yields are not high, the method is necessary for the synthesis of some compounds which were previously accessible only with difficulty.

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[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

The Condensation of 2-Furanacetic Acid with *o*-Nitrobenzaldehyde

BY E. D. AMSTUTZ AND ERVIN R. SPITZMILLER

It has only been within the past several years that the substance 2-furanacetic acid (I) has been available in quantities sufficient to permit an investigation of its chemical behavior. It was to be expected that the methylene group would resemble that in phenylacetic acid and would be capable therefore of participating in a Perkin condensation with aromatic aldehydes. This paper reports optimum conditions for the reaction of 2-furanacetic acid with *o*-nitrobenzaldehyde and the nature of the products formed.

Preliminary experiments indicated that the customary method of condensation,[1] using acetic anhydride, zinc chloride and a temperature of 120° for a period of about five hours was not well suited to the present reactants. Much decomposition occurred as evidenced by the formation of dark red tar. The yield of product, compound (II) only, was low. Eventually it was found that

TABLE I

Run[a]	*T*, °C.	Time hr.	Yields, % Crude	Compound (II)[b]	Compound III[b]
II	120- 5	6	59.2	17.8	16.8
III	60-70	6	69.7	25.1	17.5
	80-90	5			
IV	73- 5	12	100.7	42.6	23.2

[a] Run I was mentioned earlier and is not included here.
[b] Purified material.

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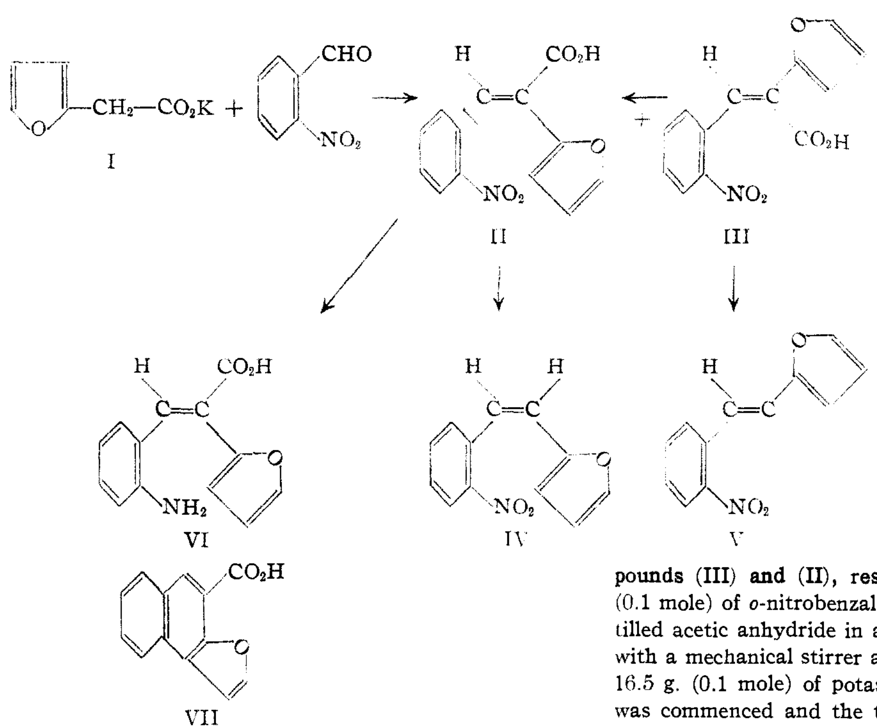
(1) Pschorr, *Ber.*, **29**, 496 (1896).



the zinc chloride was not beneficial and that lower temperatures over a longer period of time gave excellent results. Table I summarizes other conditions tried and the yields of the two products.

Separation of the isomers was easily accomplished by recrystallization of the crude reaction product from boiling water, in which the low melting form, designated as compound (III), was soluble. Compound (II), undissolved in boiling water, was purified by recrystallization from 18% acetic acid. The low melting form (III) has been assigned the structure in which the α-furyl group is *trans* to the *o*-nitrophenyl group. This substance on decarboxylation should yield a disubstituted ethylene having a higher melting point than the decarboxylation product of (II) in which the *o*-nitrophenyl and α-furyl groups have the *cis*-configuration. The experimental facts fit these expectations. Compound (III) is likewise convertible to compound (II). We were also successful in partially converting compound (IV) to a solid crystalline material but the yield was too small to permit positive identification of the solid as compound (V).

We also attempted a Pschorr ring closure with compound (VI), α-2-furyl-*o*-aminocinnamic acid, a process, which, had it been successful, would have proved conclusively the geometric configuration of the compounds (II) and (III) and would have constituted a new type of ring closure on the furan ring. The negative result of the ring closure experiments may be interpreted as further evidence of the low degree of reactivity of the β-hydrogens on the furan nucleus.

Experimental

The 2-furanacetic acid used in this work was prepared from furfural by the rhodanine method.[2] It was used in the form of the dried potassium salt.

***cis-* and *trans*-α-2-Furyl-*o*-nitrocinnamic Acids (Compounds (III) and (II), resp.).**—To a solution of 15.1 g. (0.1 mole) of *o*-nitrobenzaldehyde in 180 g. of freshly distilled acetic anhydride in a 500 cc. 3-neck flask equipped with a mechanical stirrer and reflux condenser was added 16.5 g. (0.1 mole) of potassium 2-furanacetate. Stirring was commenced and the temperature was raised over a period of about one hour to 75° where it was maintained during the reaction time of twelve hours. The solid dissolved in several hours time and the solution rapidly turned dark in color. On cooling at the end of the reaction period a rather large amount of black solid separated out. The mixture was poured out into a large beaker containing about 300 cc. of water and slowly neutralized in the cold by the addition of solid sodium carbonate and about 400 cc. of water. The alkaline solution was then filtered several times to remove most of the insoluble tarry substances. Acidification of the filtrate to congo red by the addition of cold dilute hydrochloric acid precipitated a dark green to yellow brown material which after filtration and air-drying weighed 26 g. (100.7% of the theoretical). It melted at 135–155°.

A rough separation of the mixture into its two constituents was performed by dispersal of the crude product in several hundred cc. of boiling water. This operation dissolved the low melting substance (III) and left as a residue the high melting (II). After several recrystallizations from water (III) was obtained as bright yellow crystals melting at 137.6–138.2° (cor.), yield, 6 g. (23.2%). *Anal.* Calcd. for $C_{13}H_9NO_5$: N, 5.45; neut. eq., 259. Found (III): N, 5.54; neut. eq., 261. Found (II): N, 5.50; neut. eq., 264. The higher melting substance melted at 192–192.4° (cor.), after several recrystallizations from 18% acetic acid; yield—11 g. (42.6%).[1]

Rearrangement of (III) to (II).[3]—A solution of 450 mg. of the low melting form of α-2-furyl-*o*-nitrocinnamic acid in 10 cc. of nitrobenzene was heated in an oil-bath for forty minutes at 210° with a crystal of iodine in a 25 cc. Erlenmeyer flask equipped with a reflux condenser. The cooled solution was then extracted with aqueous sodium

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(2) Plucker and Amstutz, This Journal, **62**, 1512 (1940).

(3) Rüggli and Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

carbonate. The aqueous extract was freed of nitrobenzene by extraction with ether and acidified by addition to excess cold dilute hydrochloric acid. The filtered and dried crude precipitate weighed 350 mg. and melted at 160–170°. Recrystallization from 18% acetic acid yielded 260 mg. of material which melted at 192°. The mixed m. p. with (II) was likewise 192°. Extraction of the above recrystallization mother liquors with ether yielded 50 mg. of material which was proved by the method of mixed melting points to be recovered III. Conversion under these conditions was therefore at least 58%, whereas with only twenty minutes of heating the conversion was about 40%.

Attempted Rearrangement of *cis*-α-Furyl-*o*-nitrophenylethylene to the *trans*-Isomer (IV to V).—This rearrangement was attempted by heating a sample of compound (IV) 1.59 g. in quinoline (10 cc.) for ten hours at 230°. After removal of the quinoline by extraction of an ethereal solution of the reaction products with 10% hydrochloric acid the heavy black oil was subjected to distillation under diminished pressure. At 164° and 3 mm. pressure there was obtained a light brown oil which deposited on cooling and scratching a small quantity of light yellow crystals. The amount obtained was insufficient to permit further investigation.

Decarboxylation of Compound (III).[4]—To a suspension of 0.5 g. of copper chromite catalyst[4] in 60 cc. of quinoline contained in a small beaker heated to 225° was added over a period of twenty minutes 5 g. of the low melting nitro acid (III). Heating was continued for five minutes after the addition of the acid. The resulting black liquid was cooled and poured into 300 cc. of 10% hydrochloric acid. The hydrochloric acid solution from which some oil separated was extracted with four 25-cc. portions of ether. The ethereal solutions were then combined and extracted with 10% hydrochloric acid to remove traces of quinoline, dried over anhydrous magnesium sulfate, filtered and evacuated to remove the ether. The viscous dark brown oil failed to crystallize and was therefore distilled under diminished pressure. After removal of a small forerun about 3 g. of dark red oil was collected at 200–208° and 20 mm. This material promptly solidified and was purified by recrystallization from hot dilute ethanol. Approximately 0.5 g. (15% yield) of *trans*-*o*-nitrophenyl-α-furylethylene (V) very pale yellow, melting at 92.8–93.6° (cor.) was obtained. The substance was soluble in methanol, benzene and toluene.

Anal. Calcd. for $C_{12}H_9NO_3$: N, 6.51. Found: N. 5.95.

Decarboxylation of Compound (II).—This operation was performed according to the method described above. From 4 g. of (II) there was obtained by distillation at 152–154° and 3 mm. 2.05 g. of light brown liquid soluble in ether, chloroform and warm ethanol. The substance could not be made to crystallize.

Anal. Calcd. for $C_{12}H_9NO_3$: N, 6.51. Found: N, 6.82.

Reduction of α-2-Furyl-*o*-nitrocinnamic Acid (II) to α-2-Furyl-*o*-aminocinnamic Acid (VI).—This reduction was accomplished by treatment of the nitro compound with ferrous sulfate in the presence of dilute ammonium hydroxide, the details of which have been reported elsewhere.[5] From 8 g. of (II) there was obtained 5.5 g. (78%) of the corresponding amino compound which melted at 155°. Recrystallization from hot water reduced the yield to 4 g. of pure product melting at 156°. The substance is soluble in cold alcohol, hot toluene and in hot water to the extent of 1 g. in about 250. The pure substance is salmon pink, changing upon exposure to direct sunlight to a tan yellow.

Anal. Calcd. for $C_{13}H_{11}NO_3$: N, 6.11; neut. eq., 229. Found: N, 6.18; neut. eq., 235.

In the attempted ring closure of compound (VI) to (VII) use was made of the procedure of Pschorr[1] as reported by him and as modified by Rüggli and Staub[3] and by Cassady and Bogert.[5] In all these experiments complex mixtures of substances giving positive ferric chloride tests for phenols were obtained. No homogeneous material could be isolated from them.

Summary

It has been shown that 2-furanacetic acid is capable of giving excellent yields of a mixture of two geometric isomers in the Perkin condensation with *o*-nitrobenzaldehyde. These isomers, which are readily separable, have been assigned probable configurations on the basis of the weight of experimental evidence. Attempted Pschorr ring closures on *trans*-α-2-furyl-*o*-aminocinnamic acid were unsuccessful.

BETHLEHEM, PA. RECEIVED NOVEMBER 25, 1942

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[4] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[5] Cassady and Bogert, *ibid.*, **61**, 3058 (1939).